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PATENT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	Ciampi, et al.
Appl. No.	:	10/047,460
Filed	:	January 14, 2002
For	:	METHODS OF SYNTHESIZING AN OXIDANT AND APPLICATIONS THEREOF
Examiner	:	Bos, S.J.
Group Art Unit	:	1754

RECEIVED

MAR 03 2004

DECLARATION OF PRIOR INVENTION IN THE UNITED STATES TO OVERCOME  
A CITED PATENT UNDER 37 C.F.R. 1.131

Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

I, Lee Edward Ciampi, declare and state:

1. The purpose of this declaration is to establish completion of the invention in the above-referenced application in the United States, by a date on or before December 15, 1999.
2. I am the inventor of the invention of Claims 1-3, 21-28, and 32-36 of the above-identified application and am familiar with the specification, claims, and prosecution history thereof. These claims are directed to methods of synthesizing ferrate.
3. I have read the Office Action mailed November 18, 2003, and understand that Claims 1-3, 21-28, and 32-36 have been rejected under 35 U.S.C. § 103(a) as being obvious over U.S. Patent No. 6,471,788 to Minevski et al., which is a U.S. patent based on Application No. 09/461,944, filed on December 15, 1999 ("the '944 application"). The '944 application does not include a priority claim under 35 U.S.C. § 119 or 120 to any earlier filed patent application.
4. The exhibit that accompanies this declaration, Exhibit A, was originally created at least by the date of December 15, 1999. This exhibit is submitted to establish and/or corroborate that the invention described in Claims 1-3, 21-28, and 32-36 was completed before the date of

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December 15, 1999. All of the work described in the exhibit, and elsewhere in this Declaration, was conducted in the United States of America.

5. Exhibit A is a cover letter and invoice for work conducted by Dr. David Shores. The cover letter and invoice were created and dated on a date prior to December 15, 1999. Dr. Shores was given the task of preparing a report summarizing the results of my research and the results of certain experiments conducted by others at my request and under my direction. The report prepared by Dr. Shores on the date of the invoice, and entitled "Ferrate Generation," (hereinafter referred to as "the Ferrate Report") was attached to the cover letter and invoice that was sent by Dr. Shores.

6. On page 3 of the Ferrate Report, second paragraph, lines 3-5, the difficulties associated with the use of ferrate, as understood in the then-existing literature, are identified.

7. Page 5 of the Ferrate Report, second paragraph, lines 7-12, describes in general terms how the process claimed in Claims 1-3, 21-28, and 32-36 differs from the process I had identified in the prior art. For example, the Ferrate Report states on page 5: "However, the patented processes . . . were aimed at the production of a solid, relatively pure ferrate salt, whereas the goal in the present work is to produce an aqueous stream of dissolved ferrate."

8. It was understood by those researchers working with ferrate that the main problem with successfully utilizing the full scope of ferrate's oxidizing power in a commercially viable manner was ferrate's inherent instability as a compound. Ferrate has a tendency to decompose over time. The greater the concentration of impurities in a sample of ferrate, the faster is the rate of ferrate's decomposition. For this reason, researchers prior to my invention focused their resources in developing methods of synthesizing and purifying ferrate that minimized the concentration of impurities in the final product, thereby affording ferrate a longer shelf life.

9. Contrary to the prevailing thought in ferrate research, my approach to the problem involved the generation of ferrate at a site near the site of use of ferrate, so that crude solutions of ferrate, which still possessed the full oxidizing power of freshly produced ferrate, could be used within a time-frame when decomposition had not yet taken hold.

10. My concept of on-site generation of ferrate was fully conceived prior to December 15, 1999, as evidence by a passage in the Ferrate Report at page 5, third paragraph, where the Ferrate Report states:

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The key concept by which the present project differs from earlier approaches is the idea of generating a ferrate-containing solution on-site and using it immediately. This eliminates the purification and precipitation steps necessary to make a solid ferrate salt, and immediate use of the solution also eliminates packaging and storage, which would be nearly impossible with a shelf life measured in minutes for an aqueous ferrate-containing solution. The implementation of this concept will be a reliable infusion device that will deliver a solution containing dissolved ferrate to a mixer that will rapidly disperse the ferrate into the water system. The on-site ferrate generator will be able to tailor continuous infusion rates to the demands of the water stream.

11. Accordingly, Exhibit A provides direct evidence that I conceived a physical embodiment of the invention described in Claims 1-3, 21-28, and 32-36 of the above-identified inventions, and that I was aware that this invention would work for its intended purpose at least by the date of December 15, 1999.

12. During the period at least from the preparation of the Ferrate Report, through December 15, 1999, and at least until July 14, 2000, the date on which U.S. Provisional Patent Application Serial No. 60/218,409 was filed, I diligently worked on optimizing the conditions suitable for the generation of ferrate and developing a design for a device that would generate ferrate at a site near the site of its use.

13. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful, false statements may jeopardize the validity and/or enforceability of the application and/or any patent issuing therefrom.

Dated: 2-14-04

By: Lee E. Ciampi  
Lee E. Ciampi

U.S.A.

Country of Citizenship

1322 Waltham Ave.  
Residence Belle Isle, FL 32809

# David A. Shores

455 Ripley Avenue  
Maplewood, MN 55117

612\*774-7357(Home)  
612\*625-0014 (University)  
612\*626-7246 (FAX- University)

To: Mr. Lee Ciampi  
8420 Montgomery Ct.  
Eden Prairie, MN 55347

[Redacted]

From: David A. Shores  
221 Church St., SE; Rm 112  
University of Minnesota  
Minneapolis, MN 55455

*David A. Shores*

Re: invoice for consulting

This invoice is for work done since the previous invoice [Redacted] to date. The work has included reviewing documents and data from various sources, discussions and preparing a set of recommendations for continuing tests at Outokumu Research. In addition, two analyses of material prepared by Colorado Minerals were carried out here at the University using X-ray diffraction and X-ray Photoelectron Spectroscopy.

INVOICE  
Processes for Manufacturing Iron Ferrate  
for Lee Ciampi

[Redacted]

<u>Date</u>	<u>Hours</u>	<u>Activity</u>
	1	discussions
	1	samples for analysis
	1	review data
	1.5	review data
	1	discussions
	1	prepare report
	2.5	prepare report
	2	prepare report
	1	review data
	2	review data
	2	prepare report
	1	calculations
	2	revise report
	2.5	revise report & discussions
	1	calculations
	(\$78.75)	X-ray Diffraction
	(\$90.00)	XPS analysis

Summary: 22.5 hours to [Redacted]

Total invoice: \$1434.37

Please remit total to:

David A. Shores  
455 Ripley Ave.  
Maplewood, MN 55117

Thank you.

## Ferrate Generation

### Abstract

The objectives of this study are: (1) to obtain scientific and engineering data that will assist in the design of a manufacturing process or processes to produce  $K_2FeO_4$  and/or  $Na_2FeO_4$ , and (2) to design and build a prototype reactor to demonstrate the process or processes.

## Ferrate Generation

### I. Background

Ferrates are a class of compounds in which iron is present in an anion in a high valence state (+4 to +6). Typically these compounds have been synthesized as alkali or alkaline earth salts. Numerous patents and articles have described several chemical reactions and processes to produce relatively pure ferrates, but to date none have been developed commercially. Because of their unusually high valence, these compounds are very strong oxidants, and they are unstable to varying degrees in aqueous environments and as pure solid salts.

Nevertheless, ferrates hold considerable promise for various water treatment applications owing to three important properties: (a) because of their strong oxidation potential, they have been shown to selectively oxidize, and hence aid in the removal of, hazardous chemicals and to kill certain living organisms found in water, (b) the product of the oxidation reaction is innocuous rust,  $\text{Fe(OH)}_3$ , and (c) ferrate leaves no residuals behind, because the ferrate ion eventually reacts with water to form rust. These properties offer specific advantages for treatment of drinking water and other specific advantages for the treatment of waste water, where the precipitation and filtration of undesirable chemical species is aided by the flocculation properties of the  $\text{Fe(OH)}_3$ . As an example in the latter category, the removal of arsenic makes use of both an oxidation reaction (oxidation of  $\text{As}^{+3}$  to an insoluble  $\text{As}^{+5}$ ) and the flocculation of  $\text{Fe(OH)}_3$  as an aid in filtration. Other applications making use of the high oxidizing power of the ferrate ion have also been mentioned in the literature.

Much work has been published over a period of several decades in the chemical and patent literature on the synthesis and analysis of alkali ferrates (primarily  $\text{K}_2\text{FeO}_4$  and  $\text{Na}_2\text{FeO}_4$ ). Generally, the goal of the relevant patents was to produce relatively high purity solid ferrate salts. Because of the complexity of these synthesis processes, and especially because of the difficulty of separating a relatively pure solid ferrate salt from the process solutions, the projected cost of these salts has been rather high. For the water treatment market, alternative chemicals based on chlorine have been readily available and much cheaper than

pure solid ferrate salts; hence a market for ferrate-based water treatment processes has not yet developed. However, factors other than cost, such as the recent suggestion that dangerous chemical species (e.g., "THM's") may be produced in water treatment plants by the reaction of chlorine-containing species with residual organic molecules in the inlet water stream, may serve to make ferrate-based water treatment processes more attractive. Nevertheless, the cost of ferrate salts must be reduced substantially below that corresponding to pure ferrate salts derived from processes described in patents before a water-treatment market is likely to be developed.

## II Proposed Work

The referenced patents by M. Johnson and by J. P. Deininger [1-3], as well as other information from the literature, provide the starting point for developing one or two synthesis processes appropriate for the applications of interest to Ferrox Inc. In this context, a "synthesis process" involves both the chemical reactions and the equipment to produce a ferrate-containing product stream.

This proposal offers to study the chemical synthesis processes to produce  $K_2FeO_4$  or  $Na_2FeO_4$  via three different routes: (a) the reaction of Oxone with ferric sulfate in a strongly basic solution, [3] (b) the reaction of a dissolved ferric or ferrous salt with hypochlorite in a strongly basic solution,[1, 2] and (c) the moderate temperature direct reaction of ferric oxide with  $KO_2$ . Each of these processes has been described in the literature or in patents, so the chemistry and synthesis reactions are regarded as non-proprietary. However, the patented processes for routes (a) and (b) were aimed at the production of a solid, relatively pure ferrate salt, whereas the goal in the present work is to produce an aqueous stream of dissolved ferrate. Therefore, some steps in the patented processes, such as precipitation and purification, will not be used and other steps may be altered to optimizing the yield of dissolved ferrate. Route (c) is intended to produce small quantities of  $K_2FeO_4$  for internal use in the project or to provide demonstration samples of  $K_2FeO_4$  to potential customers of Ferrox Inc.

The key concept by which the present project differs from earlier approaches is the idea of generating a ferrate-containing solution on-site and using it immediately. This eliminates the purification and precipitation steps necessary to make a solid ferrate salt, and immediate use of the solution also eliminates packaging and storage, which would be nearly impossible with a shelf life measured in minutes for an aqueous ferrate-containing solution. The implementation of this concept will be a reliable infusion device that will deliver a solution containing dissolved ferrate to a mixer that will rapidly disperse the ferrate into the water stream. The on-site ferrate generator will be able to tailor continuous infusion rates to the demands of the water stream.

Insufficient information is currently available about yields and costs and about the chemistry of the ferrate stream to allow a choice to be made between route (a) versus route (b). The role of chlorine-containing species in the ferrate product, present in route (b) and absent in route (a), may become a critical issue in that some applications may demand a chlorine-free source of ferrate. It is recommended that both routes be pursued in parallel until a winner becomes clear, or until it becomes clear that there are sufficient applications to justify supporting both routes.

## II-a Development of Synthesis Equipment

The primary goal of this project will be to build prototype devices that can continuously generate a stream of ferrate-containing solution. The two synthesis chemistries, i.e., via Oxone™ or via hypochlorite will require two different devices, but there are likely to be numerous commonalities based on solution handling , heat extraction, pumping, sensing and monitoring requirements. A patent application for a device based on the Oxone™ process has been initiated, and it is expected that further discussions will lead to either: (a) an expanded patent description to include the hypochlorite process, or (b) a bifurcation into separate patents for each process.

In general both prototype on-site generators (OSGs) will have as major components: storage tanks or bins for the reactants, a reactor section where ferrate is actually generated, heat extraction (refrigerator), pumps and valves, and computer-controlled sensing and monitoring devices. One of the key differences between OSG-Oxone™ and OSG-hypochlorite is that the former involves mixing two solids, then adding a highly basic liquid solution, whereas the latter involves mixing liquid solutions, but also involves handling highly toxic gaseous chlorine.

The following work plan is proposed:

Stage 1: Design two prototype on-site generators: an OSG -Oxone™ and an OSG - hypochlorite. Off-the-shelf components will be used as much as possible. The designed capacity will be small as appropriate for laboratory studies.

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Stage 2: Operate the two OSGs over a variety of parameter settings to determine performance characteristics, to help establish preliminary costs, and especially to identify shortcomings and opportunities for improved performance and cost savings. The yield of ferrate in the product stream will be a key measurement. We will attempt to optimize ferrate yield by varying parameters such as component ratios and temperature.

Stage 3: Design and build two improved prototype OSGs based on the experience gained in stage 2. The operating capacity, in terms of grams ferrate produced per hour, will be appropriate for a small pilot plant operation. These units will be provided to others for testing and demonstration in a water treatment laboratory to gain experience and to demonstrate efficiency of ferrate treatments. At this stage it will be necessary to incorporate appropriately high mixing rates and to be able to analyze the treated water for residual components.

Stage 4: Based on feedback and comments from the pilot plant demonstrations, continue to re-design and improve the prototype and initiate/continue design dialog with the manufacturing division of Ferrox, Inc.

The data collected from the experience with the stage 1 prototype OSGs will help support the reduction to practice component of the patent application.

#### II-a Aqueous (Oxone<sup>TM</sup> ) process

The reaction between Oxone<sup>TM</sup> (a mixture of monoperoxosulfate and K<sub>2</sub>SO<sub>4</sub>) and (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> • 9H<sub>2</sub>O) in a strong KOH solution in a chilled reactor immediately produces dissolved K<sub>2</sub>FeO<sub>4</sub>. An approximate chemical reaction involving dissolved ions can be written as:



(HSO<sub>5</sub><sup>-</sup> is the active oxidizer in Oxone<sup>TM</sup>.)

A literal interpretation of this equation would suggest the conversion of 2 moles of Fe<sup>3+</sup> into 2 moles of FeO<sub>4</sub><sup>2-</sup>. Since actual conversions are considerably less than 100%, it's clear that the actual reaction is more complex than represented

here. Nevertheless, this equation can provide initial guidance about the ratios of components and possibly help identify directions to increase yield.

The reaction and synthesis process is described in a patent by M. Johnson [3]. The patent also describes further filtration and precipitation treatments using concentrated KOH to produce relatively pure (up to 80%) K<sub>2</sub>FeO<sub>4</sub>. These latter steps will not be used in the OSG.

We have made solid K<sub>2</sub>FeO<sub>4</sub> in the laboratory following the steps described in the patent. However, the purification steps use large quantities of concentrated KOH and entail considerable losses of K<sub>2</sub>FeO<sub>4</sub> through filtration and slow decomposition. The low yields and the high cost of chemicals are certain to make the solid salt product expensive. Our current assessment is that the manufactured cost of pure K<sub>2</sub>FeO<sub>4</sub> via this process would be much too high for this product to be competitive for water treatment.

The current interest stems from using the product of the first stage of the process, without further purification, for water treatment. This product is an aqueous solution containing unreacted ferric sulfate, possibly unreacted Oxone™, potassium sulfate, KOH and about 20% dissolved K<sub>2</sub>FeO<sub>4</sub>. This solution could be used for treatment of drinking water, if made on site and used immediately. Subsequent adjustment of the pH of the treated water would probably be needed. Furthermore, this product might be more effective per lb of K<sub>2</sub>FeO<sub>4</sub> than a solid salt form, because the presence of KOH and ferric ions might retard the decomposition reaction with water as the product stream is being mixed with the untreated water.

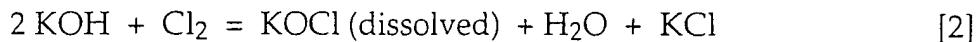
The efficiency of this product at water treatment has not yet been tested. Because K<sub>2</sub>FeO<sub>4</sub> slowly decomposes in water and because the concentrations of FeO<sub>4</sub><sup>2-</sup> applicable to many water treatment problems are in the ppm range, it is necessary that the product stream from the reactor be mixed quickly and efficiently with the process water stream. It is expected that adequately short mixing times, i.e., the time required to uniformly disperse a small amount of solution containing 20% FeO<sub>4</sub><sup>2-</sup> into a large volume of solution can be achieved. A dilution ratio of 10<sup>4</sup> to 10<sup>5</sup> with mixing times on the order of a few minutes, or less, can be obtained with the use of existing mixing strategies already in use in

water treatment plants [4]. Proper evaluation of the product will require rapid mixing so that its full potency can be applied to the water treatment reactions.

### II-b Hypochlorite process

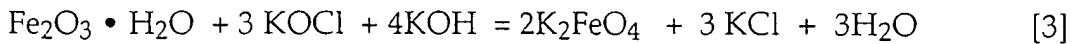
The hypochlorite process has been described several times in the literature and in patents, e.g., in [1, 2], as a method of producing relatively pure, solid K<sub>2</sub>FeO<sub>4</sub>. Following these two patents as a guide, the process may be summarized as follows:

- (1) Chlorine gas is bubbled through a strongly basic KOH solution ( $\approx$  6M) to form hypochlorite (KOCl) by the reaction:



The insoluble product KCl was removed by filtration.

- (2) Additional KOH and iron (ferric) oxide or ferric ions are added to the solution, and K<sub>2</sub>FeO<sub>4</sub> is formed by the reaction:



Deininger ([1, 2]) emphasizes the importance of the form of the iron source -  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> - and the use of a small concentration of KI (or of other such salts) to improve the rate of this reaction and improve the yield. This solution is held at about 25°C ( $\approx$  room temperature) and stirred continuously for 1 - 6 hours.

- (3) At the end of the reaction time solid K<sub>2</sub>FeO<sub>4</sub> was filtered from the slurry. It is unknown how much soluble ferrate remained in the solution. In one described example, in which KOCl was present in considerable excess over that represented in reaction [3], the wet filter cake recovered after a reaction of 1 hour was found to contain about 39% K<sub>2</sub>FeO<sub>4</sub>. After drying, the Fe content of the solid was reported as 97% FeO<sub>4</sub><sup>2-</sup>. Although there are several details that are not clear from the patent, it appears that there is a considerable potential for converting Fe<sup>+3</sup> to FeO<sub>4</sub> by KOCl.

In view of our intended use of a ferrate-containing solution instead of a solid product, several questions need to be answered, which may lead to modifications of the patent process:

- (a) Is KI needed? If so, what is the consequence of KI in the product stream for use in water treatment?
- (b) Can the rate of  $K_2FeO_4$  or  $Na_2FeO_4$  generation be increased substantially?
- (c) Is there any advantage in generating  $Na_2FeO_4$  instead of  $K_2FeO_4$ ?  $Na_2FeO_4$  is much more soluble in strongly basic solutions. This property would be a severe disadvantage in a process intended to produce a solid salt product, so  $Na_2FeO_4$  may not have been evaluated as thoroughly as  $K_2FeO_4$  in the study described in the patents. Is  $Na_2FeO_4$  as effective in water treatment?
- (d) What are the rates of conversion when the less expensive component, ferric oxide, is in excess, instead of KOCl?
- (e) Is residual KOCl (or equivalently, NaOCl) in the ferrate product stream a disadvantage for an intended application for water treatment?

We at the University of Minnesota have had essentially no practical experience with the hypochlorite process. Based on the patent descriptions we can visualize a design for a prototype OSG. However, we propose to carry out some preliminary laboratory bench-scale experiments, similar to what we have done with the Oxone<sup>TM</sup> process, to gain some familiarity with the reaction kinetics and initial yields of ferrate. This experience will help guide the design of the prototype OSG.

#### II-c Direct reaction process

The direct reaction of pure  $KO_2$  with  $Fe_2O_3$  at temperatures around  $500^\circ C$  has been shown by preliminary experiments in our laboratory to proceed quickly with quite high conversions to  $K_2FeO_4$ , providing precautions are taken to remove and exclude moisture. This approach has been described in the literature, as it is a common way to produce relatively pure ferrate compounds, e.g., for scientific characterization studies. The process appears to pose no special problems to scale-up for manufacturing. However, the high cost of pure  $KO_2$  is likely to make the cost of the product  $K_2FeO_4$  non-competitive for water treatment. It seems possible that a market for fine chemical grade  $K_2FeO_4$  would become accessible for purities of 95% to 99.9%. There is currently no known

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manufacturer producing fine chemical grade of K<sub>2</sub>FeO<sub>4</sub>. The challenge here would be to devise a purification scheme. The intended activities are:

- (1) Use the direct method with commercially purchased KO<sub>2</sub> to prepare small quantities of K<sub>2</sub>FeO<sub>4</sub> for distribution to potential customers and for use within the program.
- (2) Search the literature to determine the manufacturing method by which pure KO<sub>2</sub> is currently being produced, determine what are its likely residual contaminants, and determine what controls its current cost. Estimate a likely cost of manufacturing relatively pure K<sub>2</sub>FeO<sub>4</sub> by this process and compare this cost with other process routes for a water treatment application.
- (3) Search the literature for a purification scheme to make fine chemical-grade (99.9% pure) K<sub>2</sub>FeO<sub>4</sub>.